

California Environmental Protection Agency



Air Resources Board

Engineering and Monitoring Branch
Monitoring and Laboratory Division

SOP MLD ES07

**STANDARD OPERATING PROCEDURE FOR THE
DETERMINATION OF ACETONE AND LOW
MOLECULAR WEIGHT ALCOHOLS IN CONSUMER
PRODUCTS BY GAS CHROMATOGRAPHY-FID**

February 3, 1999, Revision 3

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

In the analysis of volatile organic compounds (VOCs) in consumer products, the percent total volatile content is determined by SOP MLD ES01. From this total is subtracted that portion of volatile material not classified as VOC, eg. water and ammonium. Several compounds have been identified as less reactive and therefore exempt from the VOC definition and is subtracted from the total volatile content, this includes acetone, ethanol (in AP/DO), methyl acetate, and perchloroethylene. To characterize the volatile content present, this procedure looks at several compounds both exempt and non-exempt. This SOP describes the determination the above compounds, low molecular weight alcohols and limonene, a common fragrance, using a capillary gas chromatograph with flame ionization detection.

The analysis for additional compounds including dichloromethane , 1,1,1-trichloroethane, and p-chlorobenzotrifluoride which are exempt, but less prevalent in the products, is described in Appendix A of this SOP and includes addition compounds generally seen in the products. The determination of these compounds uses the same column and conditions as described for the acetone. For more information see ARB Test Method 310, NIOSH Method 1400 Alcohols I, February 1984.

2 SUMMARY OF METHOD

The system consists of a Hewlett-Packard 5890 Series II with a flame ionization detector. The autosampler is an HP 6890 Series injector/controller. The data analysis is operated through the HP 3365 Series II Chemstation software.

The samples are prepared as dilutions in 1-methoxy-2-propanol as described for the Karl Fischer analysis (SOP ES03) and the GC/Water analysis (SOP ES04). An external standard calibration is made for the acetone, five alcohols (methanol, ethanol, isopropanol, 1-propanol, and isobutanol), methyl acetate, perchloroethylene, and limonene.

3 INTERFERENCES AND LIMITATIONS

With the increase in the number of compounds being identified, there may start to get overlap of the retention times. Care must be taken to make certain of the identity of the compounds, if necessary through gas-chromatography-mass spectrometry.

4 INSTRUMENTATION AND EQUIPMENT

4.1 Gas chromatographic system

Hewlett-Packard 5890 Series II with flame ionization detector (FID), HP 6890 Series Injector, GC autosampler controller.

4.1a. GC Parameters are as follows:

Oven conditions:	
Initial temperature:	35 °C
Initial time:	5.0 min
Rate:	10 °C/min
Final temperature:	200 °C
Final time:	1.0 min
Run time:	22.5 min
Oven equilibration:	0.3 min
Injector temperature:	250 °C
Detector temperature:	250°
Carrier gas (He):	10 psi (26 cm/sec)

4.1b. Column: J & W DB-624, 30 m x 0.32 mm i.d. with 1.8 μ film.

4.2 Printer Epson LQ-950

4.3 Volumetric flasks, 25 and 10 mL

4.4 Rainin pipettors, 2.5 mL and 1.0 mL with pipets

4.5 Screw-cap storage bottles-10 mL

4.6 Sartorius MCI analytical balance

4.7 GC vials and caps

5 REAGENTS AND MATERIALS

5.1 Spectrophotometric grade acetone, methanol, ethanol, isopropanol, 1-propanol, isobutanol, methyl acetate, perchloroethylene, and limonene.

5.2 1-Methoxy-2-Propanol (Aldrich #26,889-5) stored over 4A molecular sieve.

5.3 Stock standards for the 9 compounds: The stock standard is prepared gravimetrically to a concentration of 80 mg/mL. Into a 25 mL volumetric flask, weigh 2.00 g of each standard and bring to volume with MPA. The balance of the working standards are prepared from this solution.

5.4 Working standards: The working standards are prepared as follows:

<u>Concentration</u>	<u>Volume</u>
10 mg/mL	1.25 mL of 80 mg/mL to 10 mL
20 mg/mL	2.50
40 mg/mL	5.00
60 mg/mL	7.50
80 mg/mL	----

The standards are mixed well and transferred to individual screw-capped vials.

5.5 Gases, ultrahigh purity helium (He), compressed air, and hydrogen.

6 PROCEDURE

- 6.1 The samples are prepared as 1:10 dilutions in 1-methoxy-2-propanol (MPA). Using a 1.0 mL pipet, weigh to the nearest 0.1 mg an aliquot of the product into the 10 mL volumetric flask. Record the weight. Bring to volume with MPA, well and transfer to a 10 mL screw-capped storage vial.
- 6.2 Calibration: A 5 point linear regression calibration is made for all nine compounds.
- 6.3 Pipet an aliquot of each standard into a gc vial and cap.
- 6.4 The first run is an MPA blank.
- 6.5 Pipet an aliquot of each sample into appropriately labelled gc vial and cap.
- 6.6 Place vials in the autosampler.
- 6.7 In the HP Chem software, edit the SEQUENCE parameters appropriately.
- 6.8 Run the sequence.

7 QUALITY CONTROL

- 7.1 Limit of detection (LOD):

The detection limit is determined annually by running the low end standard approximately ten (10) times. The LOD is defined as: (3 x standard deviation) + absolute b.

- 7.2 A control of 25% acetone is run after the calibration and every ten (10) samples and the end of the run. The control should be within the controls limits of $\pm 3s$ of the calculated value.

APPENDIX A

Analysis for Dichloromethane and Trichloroethane

Dichloromethane, 1,1,1-trichloroethane and p-chlorobenzotrifluoride are compounds that are exempt under the consumer products regulation, but appear in only a few products. Since these compounds are currently only being found periodically, they have not been included in the protocol for routine analysis. A separate analysis for these compounds is required if they appear in the acetone basic screening. In addition to these compounds, aromatic hydrocarbons like toluene, and the xylenes are common in certain products, particularly those solvent based (paints, automotive products). Ethyl acetate is also observed in these types products and is included in this section.

The analysis for the above listed compounds is run under the same conditions as described for the acetone procedure. The method is DCM.mth and the sequence is named DCM.seq. The DCM method is loaded and the sequence consists of calibrating the instrument for the compounds, this will be a 5-point calibration as described in the procedure. The compounds and retention times is as follows:

Dichloromethane	5.109 min
Ethyl Acetate	7.660 min
1,1,1-trichloroethane	8.295 min
Toluene	11.711 min
m,p-Xylene	14.015 min
o-Xylene	14.556 min

If these compounds are present, they will appear at the designated retention times in the acetone analysis.

1. Prepare the calibration standards from the prepared stock.
2. Load DCM method and DCM sequence and run the 5 - point calibration.
3. Using the DCM method, reprocess the acetone sequence data, the presence of any of the above compounds will be quantitated.

APPENDIX B

ACETONE/ALCOHOL PROCEDURE: OPERATION OF 5890

1. Check the all gases, including the He tank. Change the tank if the pressure is down to 500 psi. Do not start run unless you have time to verify at a minimum the 40 mg standard and record the area counts. A run should not be started if it will run over a weekend.
2. The GC/Acetone analysis is run on the 5890, using injector B and detector B (FID). The procedure runs independently of the GC/water analysis, using a separate injector tower. All gas flows have been set for both methods. All that is necessary on the Acetone procedure is to ignite the FID. The air/H₂ knobs on the front panel of the GC are already on. Turn on the main valve for the air the gauge has been set. For the H₂ depress the toggle switch on the top of the H₂ generator, the psi should be around 20. Press the FID ignitor on the front of the GC.

3. **Preparation of Standards:**

Nine standards are prepared for this analysis: (from Aldrich) methanol, ethanol, acetone, isopropanol, 1-propanol, isobutanol, methyl acetate, perchloroethylene, and limonene. An 80 mg/mL stock is prepared and stored in 20 mL vials and kept in the refrigerator.

Preparation of stock:

Weigh 40.0 g of each standard into a 500 mL volumetric flask and bring to volume with MPA. Ethanol is weighed out at 42.0 g and isopropanol is weighed out at 38.0 g to correct for denatured alcohol. Aliquot into 20 ml vials, cap date, and store in the refrigerator. Record in the reagent lab notebook the date prepared, weights and analyst's initials.

4. **Working Standards:**

Remove a 20 ml vial of stock. From this solution, prepare the working standards in 10 mL volumetric flask each:

<u>Concentration</u>	<u>mL of 80 mg/mL</u>
10 mg/mL	1.25
20	2.50
40	5.00
60	7.50
80	_____

Place in screw-cap vials. Use the 2.5 ml Rainin pipettor to do the dilutions.

5. **Control Check:**

A control check of 25% acetone is analyzed after the calibration, after every 10 samples, and at the end of the run. A stock solution of 25% acetone/water/DCM check is kept in the refrigerator. The control is prepared as a 1:10 dilution. Pipet 1.0 mL of the solution into a 10 mL volumetric and bring to volume with MPA. An aliquot of this is analyzed with the samples and recorded on the control charts. If the check is not within the established control limits, re-analyze the control.

6. **Trip:**

A Trip sample of known concentration is carried out with the procedure. These samples are prepared in 20 mL vials and kept in the refrigerator. One is taken with the sample set. They are logged in the LIMS at the time of aliquoting and given separate numbers. The analyst takes the next trip sample (TS) in numerical sequence.

7. **GC conditions:**

Column: J&W DB-624 30 m x 0.32 id with 1.8 μ m film thickness

Oven Temperature:	35°
Init. Time:	5.0 min
Rate:	10°/min
Final:	200°
Final Time:	1.0 min
Injector Temperature:	250°
Detector Temperature:	250°
DET B FID ON	
EPP B:	9.5 psi at 35°
Split Ratio:	100 mL/min

8. Verify that you have loaded the acetone method in the system. In the HP CHEM station, click on Method; then click on Load. The method used is **ACETONE**. Highlight ACETONE, then press LOAD.

9. Modify the sequence as necessary. The sequence used is called **acetone**. Click on SEQUENCE, then highlight ACETONE, and load. Then click on Sequence, Edit Sequence Parameters to create a subdirectory for the data.

--Enter in Subdirectory a data file path, Yr/Mon/Day

Eg. 961016A (the letter to designate another data file if there is already one of the same date.)

10. Click on Sequence, Edit Sequence Table.

--Injector, REAR

Enter Blank, the 5 standards, checks, trip and the method and vial number.

11. Click on Sequence, Edit Sample Table, here enter the sample id number.

--Enter all samples, eg 980000058. Each sample should be in an individual tray or vial number. Use the LIMS number for the trip sample. Remember LIMS numbers are nine characters.

-- SAVE in ACETONE sequence

--PRINT Sample Log Table (See example)

Double check that everything has been entered correctly. Now ready to initiate the analysis.

12. Click on RUN CONTROL, Run Sequence.
13. Record the sequence, blank, checks, Trip, and any observations in the lab notebook.
14. Check the calibration and initial and date. It is critical that prior to allowing a run overnight that as a minimum the standards through the 40 mg are checked and verified. Record the 40 mg standard is recorded in the notebook and review prior entries before continuing. At the conclusion of the run print out the graphs.
15. Record the controls on the control chart, check that the check is in the control limits. If not re-calibrate and re-run the analysis for the out of control samples.
16. Review the chromatograms, write on the printout the weights and the corrected value, check that the MPA peak is consistently of the same height throughout the analysis. Initial and date, file the print out in a folder and place in the box labeled for acetone.

Revision History

1. Revision 2: March 10, 1998. Adjusted document font to Times New Roman 12. Inserted appendix B formerly a stand-alone document.
2. Revision 3: February 3, 1999: Addition of exempt compounds in the calibration files. This also includes modifications to Appendix A to include additional analyzes for some less common exempts and aromatic hydrocarbons.